COMPARATIVE ANALYSIS OF THE COMPOSITIONS OF THE "KERKURI" RESINS WITH DIFFERENT RATIOS OF THE M AND Q UNITS

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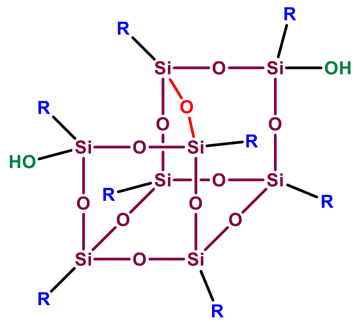
Abstract

The compositions and structures of methyl MQ resins with different M/Q ratios were studied using NMR and IR spectroscopy, as well as gel permeation chromatography (GPC). It was found that the M/Q ratio affects the molecular weight of the siloxanes under consideration and the activity of hetero- and homopolycondensation. Depending on the M/Q ratio, MQ resins can act as plasticizers or reagents.



Key words: MQ resins, siloxanes, plasticizers.

Introduction

In recent years, a large number of patents have been published on the development and application of MQ resins in different fields. Initially, MQ resins were used as additives for the production of pressure-sensitive adhesives, but each year the application scope of these siloxane materials is expanding [1]. MQ resins began to be used in construction, production of elastomers, in medicine, and cosmetology. In Russia, the production of resins was stopped in the 1990s, but their development and research continued. MQ resins are of practical interest all over the world [2]. In this communication, we studied some methyl MQ resins by different methods.

MQ resin consists of two types of units: the M units represent $Me_3SiO_{1/2}$ groups, while the Q units are $SiO_{4/2}$ groups. These units are arranged in a certain way inside the molecule [3]. The ratio of the M and Q units in a molecule allows one to obtain the products that principally differ in their properties, but have a certain gradation.

Results and discussion

All the MQ resins explored are well soluble in THF, acetone, ethanol, and chloroform and are insoluble in water. They readily mix with silicone rubbers.

The weight-average and number-average molecular weights of the resins were determined on a chromatograph equipped with a Gilson refractive index detector, using the flow rate of 1 mL/min, tetrahydrofuran as an eluent, and an Agilent MIXED-E column (up to 30 kDa). The calibration was performed using the polystyrene standards with molar masses of 580, 1280, 2940, 10110, and 28770 g/mol and polydispersity indices below 1.10 from Agilent.

The resin samples were provided by IP A. L. Filippov and were produced according to the *Specifications* (TU) 20.30.12-021-2011409497-2022.

It was found that a decrease in the theoretical M/Q ratio increases the molecular weight of the siloxane polymer, which, in turn, changes the physicomechanical and rheological properties.

The MQ resins with the theoretical M/Q ratio above 0.875 are viscous liquids, and the higher this ratio, the lower their viscosity. The MQ resins with the theoretical M/Q ratio below 0.875 are transparent crystalline substances.

It was shown that the samples with the theoretical M/Q ratio of 0.375 contain high-molecular-weight fractions with the molecular weight of 45000, the samples with the theoretical M/Q ratio of 0.5—43000, the samples with the theoretical M/Q ratio of 0.675—42000, the samples with the theoretical ratio of 0.75—58000, the samples with the theoretical M/Q ratio of 0.875—23,000, the samples with the theoretical M/Q ratio of 1—6800, and the samples with the theoretical M/Q ratio of 1.125—6000. As an example, Fig. 1 shows the GPC curve of the MQ resin with the ratio of the units of 0.875.

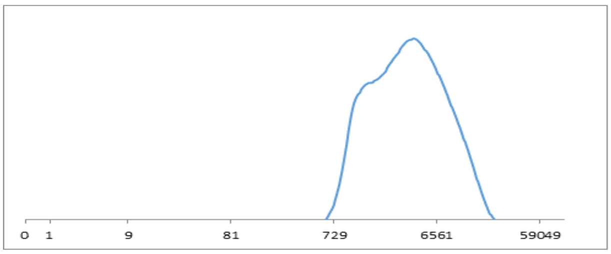


Figure 1. GPC curve of the MQ resin with the theoretical M/Q ratio of 0.875.

Table 1 presents the number-average and weight-average molecular weights as well as the polydispersity indices of the MQ resins explored.

Table 1. Molecular weight characteristics of the MQ resins explored

M/Q ratio	M_w	M_n	PDI
1.125	1864	1521	1.23
1.000	2328	1771	1.31
0.875	4600	2634	1.75
0.750	17896	7391	2.42
0.625	4653	769	6.05
0.500	3554	701	5.07
0.375	3361	702	4.79

When analyzing the GPC curves of the liquid MQ resins, it was found that the GPC curves are unimodal. The polydispersity indices were below 2 and close to 1, which allowed us to conclude that the reaction occurs by a single mechanism.

When analyzing the GPC curves of the crystalline MQ resins, it was revealed that the polydispersity indices are much higher than 2 and the GPC curves are polymodal. This implies the possibility that the product formation occurs by different mechanisms. Figure 2 shows the dependence of the polydispersity index on the theoretical ratio of the M and Q units.

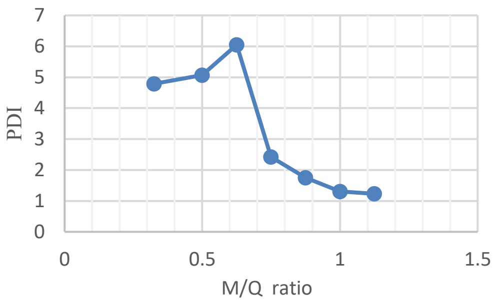


Figure 2. Dependence of the polydispersity index on the theoretical ratio of the M and Q units.

The compositions of the MQ resins were studied by IR spectroscopy with a Spectrum Two FTIR spectrometer (Perkin Elmer, USA). The spectra were recorded in the ATR mode using an artificial diamond at room temperature in the range from 4000 to 500 cm^{-1}.

Table 2. Vibration frequencies of organosilicon bonds in the MQ resins

M/Q ratio	Group		
	O–Si–O	$OSiMe_3$	OSiEt
1.125	1049	1252; 837; 754	1158; 969
1.000	1049	1252; 837; 755	1159; 970
0.875	1048	1253; 838; 755	1159; 967
0.750	1051	1253; 839; 755	1159; 967
0.675	1048	1253; 839; 755	1160; 970
0.500	1047	1254; 840; 755	1165; 970
0.375	1056	1254; 843; 756	1162; 970

Table 2 presents the frequencies of the absorption bands corresponding to the functional groups in the MQ resins. In addition to the vibrations presented in Table 2, the IR spectra of the resins showed C–H bond stretches at 2958–2980 cm^{-1} (for different MQ resins). A small shift in the resulting values compared to the theoretical ones is caused by the interaction of the functional groups with each other, which displaces the signals from the theoretical values [4].

The Fisher method was used to determine the OH groups bound with the silicon atom in the MQ resins explored. The results are presented in Table 3.

Table 3. Water content in the MQ resins explored

M/Q$_{(theor)}$	Si–OH %
1.125	0.33
1.000	0.13
0.875	0.22
0.750	0.06

Conclusions

Thus, the "KERKURI-5" MQ resins with different M/Q ratios were studied by IR and NMR spectroscopy, as well GPC and the Fisher methods. It was shown that a decrease in the M/Q ratio in the resins leads to an increase in their molecular weights. The presence of ethoxy, SiO_2, and trimethylsiloxy groups in the resins was confirmed by IR spectroscopy.

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